Table III. Ratio of the D_{2d}:D_{2h} Peak Areas

Temp, °C	D_{2d}:D_{2h}	Temp, °C	D_{2d}:D_{2h}
24	0.252	54	0.456
35	0.384	29	0.443
45	0.433	24	0.427

While two methyl resonances were observed for $Mg(acac)_2$ in $CDCl_3$, only one resonance due to ring protons was observed. If the chelate rings were not symmetric, more than one peak might be expected. However, since these protons are not affected by isomer interconversion (lying on a symmetry axis common to both conformers), only one resonance is predicted, as observed.

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Registry No. $Mg(acac)_2$, 14024-56-7; $Be(acac)_2$, 10210-64-7; $Zn(acac)_2$, 14024-63-6; $Ca(acac)_2$, 19372-44-2; $Ba(acac)_2$, 12084-29-6; $Mg(bzac)_2$, 15292-04-3; $Be(bzac)_2$, 14128-75-7; $Ca(bzac)_2$, 56513-90-7.

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Hydroxide Effects on the Electron Paramagnetic Resonance Spectrum of Aqueous Vanadyl(IV) Ion[1]

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Recently, the electron paramagnetic resonance (EPR) spectrum of the vanadyl ion (VO^{2+}) has been successfully employed as a probe of micelles,[2] anionic surfaces of acidic lipid bilayers,[3] metal-binding sites of a number of proteins,[4-9] and ATP hydrolysis.[10] In probe experiments where coordinating buffers are absent, it is often necessary to know the nature of vanadyl hydroxide species present in solution and their EPR characteristics.[6,8] We report here a quantitative EPR study of the major vanadyl hydroxide species below pH 7.

Experimental Section

Aqueous $VOSO_4$ (Alfa Inorganics) stock solution (0.0442 *M*) was prepared and standardized spectrophotometrically (molar extinction coefficient of 17.6 M^{-1} cm^{-1} at 750 mm).[5] A 200-ml amount of 4.42×10^{-4} *M* $VOSO_4$ (initial pH 2.5 (adjusted with HCl)) was titrated under nitrogen in a three-neck flask fitted with a combination calomel-glass pH electrode and rubber serum stoppers. Aliquots of standard 1.0 *N* NaOH solution were added with a microliter syringe. Samples were withdrawn periodically with a syringe and transferred to a serum stoppered nitrogen flushed quartz flat cell. The small amount of suspended vanadyl hydroxide precipitate was not removed prior to measuring the spectrum. The titration was performed twice to verify reproducibility. The sample was acidified with HCl at the end of the titration and EPR signal intensity measured to check for possible oxidation of the vanadyl ion. The EPR intensity was unchanged from before. Spectra were recorded on a Varian E-4 spectrometer operating at X-band and tuned according to procedures given in reference 9. The temperature was 25 ± 2°C.

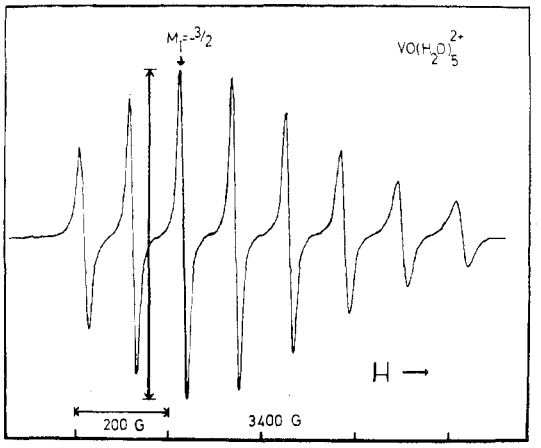

Figure 1. First-derivative isotropic EPR spectrum of $VO(H_2O)_5^{2+}$. The signal height of the $M_I = -3/2$ line used in determination of $[VO^{2+}]_{EPR}$ is indicated.

Results and Discussion

The EPR spectrum of $VO(H_2O)_5^{2+}$ is shown in Figure 1. The eight lines arise from the vanadium nuclear spin $I = 7/2$. The first-derivative peak-to-peak intensity of the $M_I = -3/2$ line (notation assumes a negative nuclear hyperfine coupling constant) was used to determine the concentration of EPR-detectable vanadyl species, hereafter referred to as $[VO^{2+}]_{EPR}$. Such a procedure is valid if the unknown and standard samples are the same chemical species in the same matrix.[9] A double integration of the first-derivative line is not required in this instance. Figure 2 shows the standard curve.

In Figure 3 the marked decrease in the vanadyl EPR intensity with increasing pH is presented. Three linear regions are observed which correspond to the formation of different hydroxide species. The equilibria which can be used to explain the data in Figure 3 are

$$VO^{2+} + H_2O \overset{K_{1,1}}{\rightleftharpoons} VOOH^+ + H^+ \quad (1)$$

$$2VO^{2+} + 2H_2O \overset{K_{2,2}}{\rightleftharpoons} (VOOH)_2^{2+} + 2H^+ \quad (2)$$

$$VO^{2+} + 2OH^- \overset{K_{sp}}{\rightleftharpoons} VO(OH)_2\downarrow \quad (3)$$

For simplicity coordinated water has been omitted from the equations.

Jones and Ray[11] measured the pH of pure vanadyl sulfate in the concentration range 1×10^{-4} to 0.5 *M*. Their data have been subsequently treated by Meites[12] to obtain $K_{1,1} = 4.4 \times 10^{-6}$ for the formation of $VOOH^+$ via eq 1.

Both free VO^{2+}, i.e., $VO(H_2O)_5^{2+}$, and $VOOH^+$ are paramagnetic; however, over most of the pH range studied the $VOOH^+$ species represents only a small fraction of the total contribution to the observed EPR signal. We were never able to observe resolved spectra due to free VO^{2+} and $VOOH^+$ with room-temperature or frozen-solution (pH 4.5) samples.

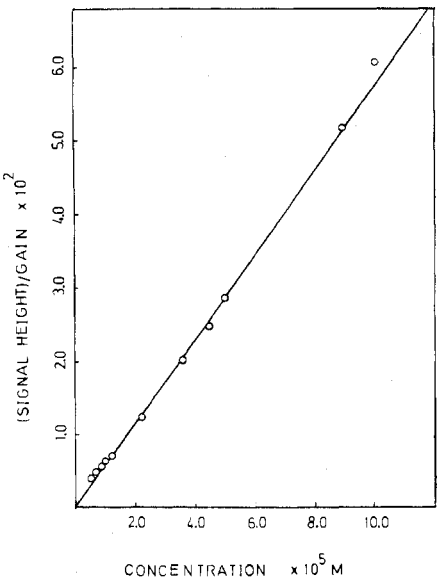

Figure 2. The VO^{2+} ion standard curve: EPR signal height divided by the instrument gain setting vs. VO^{2+} concentration in 1.2 N HCl. Power setting 100 mW; modulation amplitude 10 G.

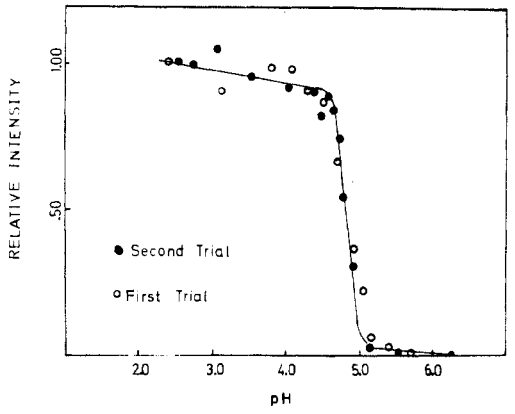

Figure 3. Relative EPR intensity of the spectrum in Figure 1 as a function of pH.

Evidence for more than one species is reflected in a very small but real variation in the relative intensities of the $M_I = -3/2$ and $M_I = -1/2$ lines. At pH ~2.5 the former line is slightly more intense than the latter (Figure 1). At pH ~5 they are equally intense. This represents less than 0.5-G change out of 11 G in the peak-to-peak width of the $M_I = -3/2$ line. At most this would contribute about a 10% error to the concentrations measured from the signal height of the first-derivative curve.

If we assume that VO^{2+} and $VOOH^{+}$ exhibit similar relaxation behavior (line widths) and have similar g values and hyperfine splittings, then we can write $[VO^{2+}]_{EPR} = [VO^{2+}]_{free} + [VOOH^{+}]$ where $[VO^{2+}]_{EPR}$ is obtained from the observed EPR signal intensity (see Figures 1 and 2). The concentration of free VO^{2+} is then given by

$$[VO^{2+}]_{free} = [VO^{2+}]_{EPR} \Big/ \frac{1 + 4.4 \times 10^{-6}}{[H^+]} \qquad (4)$$

The curve fitting of the data in Figures 4 and 5 is improved by taking into account the contribution of $VOOH^{+}$ to the observed EPR signal through eq 4.

The equilibrium constant expression for eq 2 can be arranged to give

$$[(VOOH)_2^{2+}]/[VO^{2+}]_{free}^{2} = K_{2,2}/[H^+]^2 \qquad (5)$$

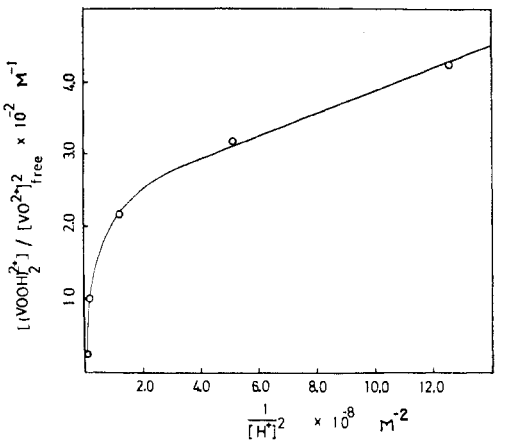

Figure 4. Determination of the equilibrium constant, $K_{2,2}$, for the formation of $(VOOH)_2^{2+}$: $[(VOOH)_2^{2+}]/[VO^{2+}]_{free}^{2}$ vs. $1/[H^+]^2$. The slope in the linear region is equal to $K_{2,2}$. (Data used is that of the second titration.)

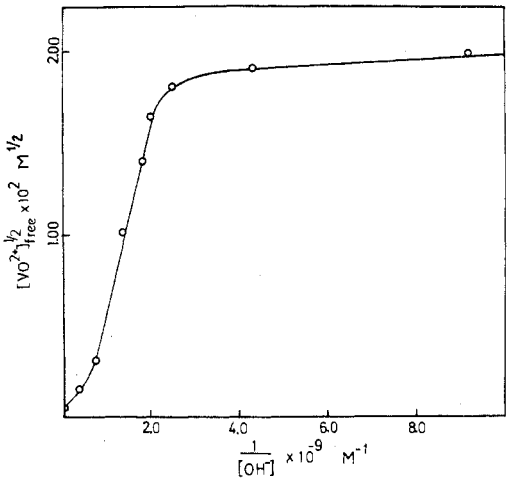

Figure 5. Determination of the K_{sp} for $VO(OH)_2$ formation: $[VO^{2+}]_{free}^{1/2}$ vs. $1/[OH^-]$. The steep slope is equal to $K_{sp}^{1/2}$. (Data used is that of the second titration.)

where $[(VOOH)_2^{2+}] = [VO^{2+}]_{total} - [VO^{2+}]_{EPR}$. $[VO^{2+}]_{free}$ is obtained from eq 4.

In Figure 4 the data are plotted according to eq 5. The linear region of the curve at high $1/[H^+]^2$ values (low pH) has a slope $K_{2,2} = 1.5 \times 10^{-7}$ M. This is in good agreement with the value of $K_{2,2} = 1.66 \times 10^{-7}$ M obtained by Rossotti and Rosotti[13] for $VO(ClO_4)_2$ in 1 M $NaClO_4$ by potentiometric and spectrophotometric measurements. Surprisingly, the ionic strength has little effect on $K_{2,2}$ in accord with the results of Lutz and Wendt.[14]

The sharply curved portion of Figure 4 is due to the appearance of a $VO(OH)_2$ precipitate, the stoichiometry of which has been confirmed by pH titration with standard base. The equilibrium constant expression for eq 3 can be rearranged to give

$$[VO^{2+}]_{free}^{1/2} = K_{sp}^{1/2}/[OH^-] \qquad (6)$$

In Figure 5, the data are plotted according to eq 6. The linear portion of the steeply sloped portion of the curve gives $K_{sp}^{1/2}$ from which we obtain $K_{sp} = (1.08 \pm 0.03) \times 10^{-22}$ M^3. The only literature value[13] available for comparison is an estimate, $K_{sp} \approx 10^{-23}$.

We conclude that the initial slow drop in EPR signal intensity in Figure 3 is due to the formation of $(VOOH)_2^{2+}$ and the subsequent sharp drop in the intensity arises from

$VO(OH)_2$ precipitation. $(VOOH)_2^{2+}$ and $VO(OH)_2$ are EPR silent at room temperature presumably because of their polynuclear structures. The gentle slope between pH 5.0 and 6.0 is probably due to the onset of amphoterism, e.g., $VO(OH)_3^-$ formation, which offsets the formation of $VO(OH)_2$.

At a pH of approximately 6.7 the solution starts becoming a golden brown color indicative of formation of a new species. As the pH is raised well into the alkaline range, the $VO(OH)_2$ precipitate dissolves. At pH 11.5 with no precipitate present a strong eight-line EPR spectrum with $A_0 = 87.3 \times 10^{-4}$ cm^{-1} and $g_0 = 1.969$ is observed. These values are in good agreement with those reported for the recently well-characterized $VO(OH)_3^-$ species.[15]

In protein studies at physiological pH in the absence of chelating buffers, one does not observe an EPR spectrum of VO^{2+} unbound to the protein. Our studies indicate that under these conditions most of the uncoordinated vanadyl ion exists as a suspension of $VO(OH)_2$.

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Registry No. $VOSO_4$, 27774-13-6; NaOH, 1310-73-2; $VO(H_2O)_5^{2+}$, 15391-95-4; $VO(OH)_2$, 30486-37-4.

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Rapid Reaction of Dimethyl Sulfoxide with Nitratopentaaquochromium(III) Ion[1,2]

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The replacement of water in the first coordination shell around chromium(III) in hexaaquochromium(III) ion by dimethyl sulfoxide is very slow, having a half-time of ~380 hr at 25° at 0.705 mole fraction of dimethyl sulfoxide.[4] It is interesting to report, therefore, that this same process (replacement of coordinated water by dimethyl sulfoxide) occurs for nitratopentaaquochromium(III) ion with a half-time of ~10 sec at 25° at 0.004–0.04 mole fraction of dimethyl sulfoxide.

Table I. Rate of Replacement of Water in $Cr(OH_2)_5ONO_2^{2+}$ by Dimethyl Sulfoxide (25°, $[Cr^{III}] = 0.016$ *M*)[a]

Z[b]	$10^2 k_{obsd}$[c]/sec^{-1}	Z[b]	$10^2 k_{obsd}$[c]/sec^{-1}
0.0036[d]	7.9 ± 0.4	0.034	8.0 ± 0.3
0.012	6.9 ± 0.5	0.045[e]	8.6 ± 0.3

[a] $k_{obsd} = -\mathrm{d} \ln (A_\infty - A)/\mathrm{d}t$. [b] Z = mole fraction of dimethyl sulfoxide in solvent, calculated with no allowance for solute species. [c] Three to five runs at each set of concentration conditions. [d] $[Cr^{III}] = 0.0197$ *M*. [e] At this solvent composition, other concentrations of chromium(III) were studied; at 0.0087 *M* Cr^{III}, $10^2 k = 9.4 \pm 1.3$ sec^{-1}; at 0.0035 *M* Cr^{III}, $10^2 k = 10.4 \pm 0.3$ sec^{-1}.

Labilizing effects of other coordinated oxy anions are known for reactions of chromium(III),[5-8] but the real precedent for the present study was the remarkable labilizing effect of nitrate ion upon the rate of loss of ammonia by nitratopentaamminechromium(III) observed by Guastalla and Swaddle.[9] In this study the two isomeric aquodihydroxytriamminechromium(III) ions are produced but only *cis*-aquohydroxytetraamminechromium(III) ion is produced. These authors suggest that ammonia located cis to the coordinated nitrate ion is displaced by the nitrate to produce a transient bidentate nitrato intermediate which opens with introduction of water into the coordination shell. This loss of ammonia by nitratopentaamminechromium(III) ion is powers of 10 faster than the corresponding reaction of hexaamminechromium(III) ion. The rapid changes which occur when nitratopentaaquochromium(III) ion (hereafter called nitratochromium(III) ion) is added to acidic aqueous dimethyl sulfoxide are reactions analogous to those observed by Guastalla and Swaddle.[9]

Experimental Section

Reagents. Hexaaquochromium(III) perchlorate was prepared from reagent grade chromium trioxide and hydrogen peroxide as already described.[4] Nitratochromium(III) ion in perchloric acid solution was prepared as described by Swaddle.[10] Reagent grade Dowex 50W resin in the hydrogen ion form was treated before use as described earlier.[11] Other chemicals were reagent grade and were used without further purification.

Spectral Measurements. Upon adding an acidic aqueous solution of nitratochromium(III) ion to acidic aqueous dimethyl sulfoxide, a rapid color change (gray-blue to green) occurs. Coordinated nitrate is lost in a much slower reaction. The spectra of solutions of various composition taken after the rapid chemical change are consistent with substitution of water by dimethyl sulfoxide in the inner coordination shell of nitratochromium(III) ion. Positions of maxima and corresponding molar absorbancy index values for the two peaks in the visible region of the spectrum for various solvent mixtures [given as mole fraction of dimethyl sulfoxide, λ_{max} (nm), $\tilde{a}$ (=(log (I_0/I))/($[Cr^{III}]$ × cell length)] are as follows: 0.0104, 410 (19.9), 578 (17.2); 0.0215, 414 (21.0), 582 (18.1); 0.0395, 416 (22.1), 588 (18.9); 0.0816, 423 (24.5), 599 (21.9); 0.144, 429 (27.2), 607 (24.9); 0.276, 436 (30.2), 616 (28.2); 0.374, 438 (32.4), 618 (30.8); 0.600, 442 (35.1), 622 (33.5).

Kinetic Measurements. Two types of kinetic measurements have been made. The rapid changes which are the primary subject of this note were studied using a Durrum stopped-flow spectrophotometer with a Kel-F mixing block and a 2-cm optical path. In these experiments, equal volumes of (1) an aqueous solution of chromium(III) perchlorate and perchloric acid (1.00 *M*) and (2) a 1.00 *M* perchloric acid in a binary dimethyl sulfoxide–water solvent mixture were mixed. The spectral change followed at 440 nm conformed to first-order kinetics, log $(A_\infty - A_t)$ being a linear function of time. Runs over a fivefold range of concentrations of chromium(III) (0.0163–0.0035 *M*) gave within experimental error the same value of k_{obsd}, the first-order rate constant for the approach to equilibrium ($k_{obsd} = \mathrm{d} \ln (A_\infty - A_t)/\mathrm{d}t$. Values of k_{obsd} are presented in Table I.

Much slower than this rapid change was the loss of nitrate co-